



Patent
Attorney Docket No. 3028.1US (96-767.1)

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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE
BEFORE THE BOARD OF PATENT APPEALS AND INTERFERENCES

Serial No.: 09/358,940 Group Art Unit No.: 1765
Filing date: July 22, 1999 Examiner: V. Perez-Ramos
For (title): HIGH SELECTIVITY BPSG TO TEOS ETCHANT

TRANSMITTAL OF APPEAL BRIEF (PATENT APPLICATION — 37 C.F.R. § 192)

Commissioner of Patents
Washington, D.C. 20231

Sir:

1. Transmitted herewith in triplicate is the APPEAL BRIEF in this application with respect to the Notice of Appeal filed on August 15, 2001.

2. STATUS OF APPLICATION

This application is on behalf of

- ☒ other than a small entity
☐ small entity
verified statement:
☐ attached
☐ already filed

3. FEE FOR FILING APPEAL BRIEF

Pursuant to 37 C.F.R. § 1.17(f) the fee for filing the Appeal Brief is:

- | | |
|---|-------|
| <input type="checkbox"/> small entity status | \$155 |
| <input checked="" type="checkbox"/> other than a small entity | \$310 |

4. EXTENSION OF TIME

- ☐ A petition for Extension of Time for a month extension of time for filing the Appeal Brief is enclosed.

5. FEE PAYMENT

- ☒ Check No. 1078 is enclosed in payment of the fee for filing the Appeal Brief plus any extension of time for which a petition has been filed. Please charge this fee to deposit account No. 20-1469 (a duplicate copy of this notice is enclosed—see below).

Any additional appeal fees which are not otherwise submitted herewith or which are insufficient should be charged to deposit account no. 20-1469. A duplicate copy of this notice is enclosed. Please address all communications in connection with this appeal to the address indicated below.

Respectfully submitted,

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Date: September 18, 2001
Enclosures: As identified above
KWP/dlm

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SEP 26 2001

TC 1700



PATENT

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE
BEFORE THE BOARD OF PATENT APPEALS AND INTERFERENCES**

In re Application of:

Lee et al.

Serial No.: 09/358,940

Filed: July 22, 1999

For: HIGH SELECTIVITY BPSG TO TEOS
ETCHANT

Examiner: V. Perez-Ramos

Group Art Unit: 1765

Attorney Docket No.: 3028.1US (96-767.1)

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APPEAL BRIEF

Commissioner for Patents
Washington, D.C. 20231

**BOARD OF PATENT APPEALS
AND INTERFERENCES**

Attention: Board of Patent Appeals and Interferences

Sirs:

This brief is submitted in triplicate and in the format of 37 C.F.R. § 1.192(c). A check in the amount of \$310.00 for the fee under 37 C.F.R. § 1.17(c) for filing a brief in support of an appeal is enclosed.

REAL PARTY IN INTEREST

The real party in interest is Micron Technology, Inc., a corporation of the State of Delaware, having a place of business at 8000 South Federal Way, Boise, Idaho 83707-0006, the assignee of the entire right, title and interest for the present application in the United States and all foreign countries.

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RELATED APPEALS AND INTERFERENCES

There are no appeals or interferences known to appellant related to the pending appeal that will directly affect, be directly affected by, or otherwise have a bearing on the decision in the pending appeal of the Board of Appeals and Interferences.

STATUS OF CLAIMS

Claims 1 through 4 and 6 through 15 are currently pending in the application and stand rejected.

No claims are allowed.

The rejection of claims 1 through 4 and 6 through 15 are being appealed.

STATUS OF AMENDMENTS

All amendments to the claims have been entered.

SUMMARY OF THE INVENTION

The present invention relates to an organic acid/fluoride-containing solution etchant formulation having high selectivity for BPSG to TEOS and methods for its use in the production of semiconductor devices. Hydrofluoric acid is a known etchant for etching BPSG and TEOS. However, it has been found that the addition of an organic acid (such as acetic acid, formic acid, and oxalic acid) to a fluoride-containing solution (such as hydrofluoric acid and ammonium fluoride (preferably 40% NH_4F in water)) dramatically increases selectivity of BPSG to TEOS.

Etchants were formulated from glacial acetic acid (99.7% by weight in water) and hydrofluoric acid (49% by weight in water). The results (etch rate, selectivity and uniformity) of various etchant formulations are presented in Table 1, as follows:

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TABLE 1

Etchant (vol. ratio glacial acetic acid to 49% HF)	Etching rate through TEOS (Å/min)	Etching rate through BPSG (Å/min)	BPSG Standard Deviation (%)	Selective ratio (BPSG/TEOS)
200:1	2.2	59	0	27
100:1	4.6	193	2.4	42
50:1	11.6	638	13.7	55

As it can be seen from Table 1, the selectivity and uniformity increased with increasing hydrofluoric acid concentration. The preferred etchant to obtain high selectivity and good uniformity is 100:1 volume ratio of 99.7% glacial acetic acid to 49% hydrofluoric acid. However, it is believed that etchant ratios ranging from 1:1 to 500:1 will achieve adequate selectivity.

FIGs. 1-5 illustrate a technique for utilizing an etchant of the present invention in the formation of an opening in a BPSG layer. FIG. 1 illustrates an intermediate structure 100 comprising a substrate 102 having a first side 104 with a first barrier layer 106 of TEOS applied thereover. A second barrier layer 108 of BPSG is deposited over the first TEOS barrier layer 106.

A nitride layer 110 is patterned over the second barrier layer 108 of BPSG and has at least one opening 112, as shown in FIG. 2. The second barrier layer 108 of BPSG is etched with an etchant of the present invention to form a partial opening 114. Since the etchant of the present invention is selective to BPSG, the etch effectively ceases at the first barrier layer 106 of TEOS, as shown in FIG. 3. The first barrier layer 106 of TEOS is then etched with a less aggressive etchant, such as a TMAH / hydrofluoric acid mixture or a 35-40% by weight ammonium fluoride / 4-6% by weight phosphoric acid solution in water, which is less damaging to the substrate 102, to form a full opening 120, as shown in FIG. 4. The nitride layer 110 is stripped, as shown in FIG. 5.

The etchant of the present invention can be utilized in any etching situation where selectivity of BPSG to TEOS barrier layers is desired, such as contact openings, container etching, and the like.

Furthermore, the etchant of the present invention can be utilized in processes, such as a double side container process, wherein no masking step is required.

ISSUES

A. Whether claims 1 through 4 and 6 through 15 are unpatentable under 35 U.S.C. § 103(a) over U.S. Patent 5,300,463, issued, April 5, 1994 to Cathey et al. (hereinafter “the Cathey reference”).

GROUPING OF THE CLAIMS

Group 1. Claims 1 through 4 and 6 through 8. For purposes of this appeal, claims 2 through 4, and 7, stand and fall with claim 1. Claims 6 and 8 stand, but do not fall with claim 1.

Group 2. Claims 9 through 15. For purposes of this appeal, claims 10 through 12 stand and fall with claim 9. Claims through 13 through 15 stand, but do not fall with claim 9.

ARGUMENT

Authorities Relied Upon

Appellants submit that three criteria must be met for a *prima facie* case of obviousness to be present under 35 U.S.C. § 103. First, there must be some suggestion or motivation, either in the references themselves or in the knowledge generally available to one of ordinary skill in the art, to modify the reference or to combine the reference teachings. Second, there must be a reasonable expectation of success. Third, the prior art reference or combination of the references must teach or suggest all the claim limitations. The teaching or suggestion to make the claimed combination and the reasonable expectation of success must both be found in the prior art, and not based on appellants' disclosure. MPEP §2143.

A prior art reference “must be considered in its entirety, i.e., as a whole, including portions that would lead away from the claimed invention.” MPEP §2141.02.

Appellants respectfully submit that Examiner is improperly applying an “obvious to try” rationale in this case. (Office Action, page 2; “variation of the process parameters is obvious and expected”). The “obvious to try” standard is inappropriate under §103:

In some cases, what would have been ‘obvious to try’ would have been to vary all parameters or try each of numerous possible choices until one possibly arrived at a successful result, where the prior art gave either no indication of which parameters were critical or no direction as to which of many possible choices is likely to be successful. . . . In other words, what was ‘obvious to try’ was to explore a new technology or general approach that seemed to be a promising field of experimentation, where the prior art gave only general guidance as to the particular form of the claimed invention or how to achieve it.

MPEP § 2145 (citations omitted).

To establish *prima facie* obviousness of a claimed invention, all the claim limitations must be taught or suggested by the prior art. *In re Royka*, 490 F.2d 981, 180 USPQ 580 (CCPA 1970). All words in a claim must be considered in judging the patentability of that claim against the prior art. *In re Wilson*, 424 F.2d 1382, 165 USPQ 494, 496 (CCPA 1970).

35 U.S.C. §103

A. Claims 1 through 4 and 6 through 15 were rejected under 35 U.S.C. §103(a) over the Cathey reference.

Appellants submit that the proposed Cathey reference fails to establish a *prima facie* case of obviousness. Three criteria must be met for a *prima facie* case of obviousness to be present under 35 U.S.C. § 103. First, there must be some suggestion or motivation, either in the references themselves or in the knowledge generally available to one of ordinary skill in the art, to modify the reference or to combine the reference teachings. Second, there must be a reasonable expectation of success. Third, the prior art reference or combination of the references must teach or suggest all the claim limitations. The teaching or suggestion to make the claimed combination and the reasonable expectation of success must both be found in the prior art, and not based on appellants' disclosure. MPEP §2143.

Cited Reference

The Cathey reference discloses a method of utilizing and etching SiO₂ in the processing of semiconductor wafers. The method includes utilizing an acid solution comprising at least two different mineral (inorganic) acids in a selected ratio to one another, one of the inorganic acids being HF. The Cathey reference discloses that the solution comprising at least one inorganic (mineral) acid and HF selectively etches a doped SiO₂ layer. The Cathey reference further discloses that acetic acid may be included in the solution and provides an example wherein acetic acid is provided in a 2:1 ratio with HF. However, the Cathey reference also states, “[a]cetic acid is a known prior art component in wet acid etching which provides bath stabilization and extends bath life. Such does not constitute a part of this invention, nor is it necessary in the invention.” (Cathey, col. 2, lines 49-53.)

Argument for Patentability of Claimed Invention

Appellants submit that claims 1 through 4 and 6 through 15 are clearly allowable over the Cathey reference under 35 U.S.C. § 103. Appellants submit that the Cathey reference fails to teach or suggest every limitation of the presently claimed invention. By way of contrast with the Cathey reference, independent claim 1 recites an etchant solution comprising “an organic acid and a fluoride-containing solution provided in a selected volumetric ratio relative to one another, wherein the selected volumetric ratio of the organic acid to the fluoride-containing solution is about 10:1 to about 500:1.”

The Cathey reference discloses acid solution comprising at least two different mineral (inorganic) acids in a selected ratio to one another, one of the inorganic acids being HF. The Cathey reference further discloses that acetic acid may be included in the solution and provides an example wherein acetic acid is provided in a 2:1 ratio with HF. However, the Cathey reference also states, “[a]cetic acid is a known prior art component in wet acid etching which provides bath stabilization and extends bath life. Such does not constitute a part of this invention, nor is it necessary in the

invention.” (Cathey, col. 2, lines 49-53.). Appellants respectfully submit that no motivation exists to modify the Cathey reference to incorporate an **increased** amount of *organic* acid into the solution.

The Examiner states that it would have been obvious to modify Cathey’s solution by utilizing a volumetric ratio in the range of 10:1 to 500:1 range, because “the variation of process parameters is obvious and expected from one skilled in the art”, and because, “as Cathey discloses a higher HF content in the solution would result in a higher etch rate, and high etch rates are highly desirable during semiconductor manufacturing.” (Paper No. 14, page 2).

Appellants respectfully submit that Examiner’s argument describes a solution exactly opposite the present invention. Cathey’s solution discloses a ratio of acetic acid to HF of 2:1. By way of contrast, independent claim 1 recites a volumetric ratio of organic acid to fluoride containing acid between about 10:1 to 500:1. Thus, appellants are *not increasing the content of HF* in the solution as compared to the Cathey reference. Instead, the present invention increases the amount of *organic acid* in the solution relative to the fluoride containing solution; **the concentration of HF (fluoride containing solution) does not increase**. Therefore, Examiner’s statement that it would have been obvious to increase the amount of HF in the solution is immaterial to examination of the present invention.

Examiner has misstated appellants’ arguments in the Response to Arguments. (Paper No. 14, pages 3-4). Appellants submit no motivation exists in the Cathey reference to **increase** the amount of acetic acid (organic acid) in the solution. The Cathey reference explicitly states acetic acid is not a part of the invention and as such, one of ordinary skill in the art would not be motivated to **increase** the amount of acetic acid in the etchant solution. (Cathey, col. 2, lines 49-53). A prior art reference “must be considered in its entirety, i.e., as a whole, including portions that would lead away from the claimed invention.” MPEP §2141.02. The examiner expressly states that Cathey suggests increasing the amount of HF relative to the acetic acid (which is the **opposite** of the present invention)(Paper No. 14, page 4). In this respect, the Cathey reference clearly teaches away from *increasing the amount of acetic acid* (organic acid) in the etchant solution.

Appellants respectfully submit that Examiner is improperly applying an “obvious to try” rationale in this case. (Office Action, page 2; “variation of the process parameters is obvious and expected”). The “obvious to try” standard is inappropriate under §103:

In some cases, what would have been ‘obvious to try’ would have been to vary all parameters or try each of numerous possible choices until one possibly arrived at a successful result, where the prior art gave either no indication of which parameters were critical or no direction as to which of many possible choices is likely to be successful. . . . In other words, what was ‘obvious to try’ was to explore a new technology or general approach that seemed to be a promising field of experimentation, where the prior art gave only general guidance as to the particular form of the claimed invention or how to achieve it.

MPEP § 2145 (citations omitted).

In this case, appellants respectfully submit that it would not have been obvious to modify (increase) the amount of acetic acid in the Cathey reference as the reference teaches that acetic acid is merely a bath stabilizer and not a critical component of the etchant solution. Further, the Cathey reference lacks any teaching or suggestion that increasing the amount of acetic acid will affect the etch rate and selectivity ratio of the solution as described in Table 1 of the current application. (Cf. Table 1 of the present invention with Cathey, col. 2, lines 54-60). As such, appellants respectfully submit the Cathey reference does not render independent claim 1 of the present invention obvious.

Similarly, appellants assert that there can be no showing of a reasonable expectation of success to establish a *prima facie* case of obviousness under 35 U.S.C. § 103 based upon the cited reference. The Cathey reference teaches “[a]cetic acid is a known prior art component in wet acid etching which provides bath stabilization and extends bath life. Such does not constitute a part of this invention, nor is it necessary in the invention.” (Cathey, col. 2, lines 49-53.) As such, no evidence exists, in either the Cathey reference or the art, that the modification of the Cathey reference to increase the amount or an organic acid, such as acetic acid, would be successful. Therefore, any rejection of the present invention based upon the cited prior art cannot establish a *prima facie* case of obviousness under 35 U.S.C. § 103. As such, independent claim 1, and all dependent claims therefrom, are allowable.

To establish *prima facie* obviousness of a claimed invention, all the claim limitations must be taught or suggested by the prior art. *In re Royka*, 490 F.2d 981, 180 USPQ 580 (CCPA 1970). All words in a claim must be considered in judging the patentability of that claim against the prior art. *In re Wilson*, 424 F.2d 1382, 165 USPQ 494, 496 (CCPA 1970). Appellants respectfully submit that the Cathey reference does not teach or suggest every limitation of the present invention.

Examiner acknowledges the Cathey reference does not teach or suggest a solution wherein an organic acid is in a volumetric ratio with a fluoride-containing solution at about 10:1 to about 500:1. (Paper No. 14, page 2). Instead, the Cathey reference discloses that acetic acid (an organic acid) is not a necessary component of the invention. Further, the Cathey reference only discloses organic acid in a volumetric ratio of 2:1 with HF; not "10:1 to about 500:1". (Cathey, col. 2, lines 49-53). As Cathey does not teach or suggest every element of claim 1 as proposed to be amended, Cathey does not obviate the presently claimed invention. As such, claim 1, is allowable.

Claims 2 through 4 and 6 through 8 are each allowable as depending, either directly or indirectly, from claim 1.

Claim 6 is further allowable as the Cathey reference does not teach or suggest an etchant comprising acetic acid in a volumetric ratio with hydrofluoric acid at about 10:1 to about 100:1. As stated, no motivation exists to modify the Cathey reference to increase the amount of acetic acid in the etching solution. Further, as Cathey teaches that acetic acid is not a part of the invention, appellants respectfully submit that Cathey teaches away from increasing the amount of acetic acid as compared to hydrofluoric acid.

Claim 8 is further allowable because the Cathey reference does not teach or suggest an etchant solution exhibiting a selectivity ratio of borophosphosilicate glass to tetraethyl orthosilicate between about 27:1 and 55:1. The examiner acknowledges the Cathey reference does not disclose a BPSG to TEOS selectivity ratio in the range of 27:1 to 55:1. (Paper No. 14, page 3). Appellants respectfully disagree with Examiner's conclusion that "the Cathey solution must also provide the same BPSG to TEOS selectivity ratio, as Cathey's etchant solution is similar to Appellant's claimed solution." (Paper No. 14, page 4).

The Cathey reference discloses an etchant solution comprising 840 ml H₂SO₄, 960 ml H₂O, 30 ml HF and 60 ml acetic acid. (Cathey, col. 2, lines 43-45). ***The Cathey reference expressly states that this solution has a BPSG to TEOS selectivity ratio of only 6.3:1; not 27:1 to 55:1.*** (Cathey, col. 2, lines 58-59). Further, the Cathey reference lacks any suggestion that increasing the amount of acetic acid will affect the etch rate and selectivity ratio of the solution as described in Table 1 of the current application. (Cf. Table 1 of the present invention with Cathey, col. 2, lines 54-60). Clearly, the solution of the Cathey reference does not possess a similar selectivity ratio as the etchant solution of the presently claimed invention.

Independent claim 9 of the present invention recites an etchant solution comprising an organic acid and a fluoride-containing solution, “wherein the etchant solution exhibits a selectivity ratio of borophosphosilicate glass to tetraethyl orthosilicate between about 27:1 and 55:1.” The examiner acknowledges the Cathey reference does not disclose a BPSG to TEOS selectivity ratio in the range of 27:1 to 55:1. (Paper No. 14, page 3). Appellant respectfully disagrees with Examiner’s conclusion that “the Cathey solution must also provide the same BPSG to TEOS selectivity ratio, as Cathey’s etchant solution is similar to Appellant’s claimed solution.” (Paper No. 14, page 4).

The Cathey reference discloses an etchant solution comprising 840 ml H₂SO₄, 960 ml H₂O, 30 ml HF and 60 ml acetic acid. (Cathey, col. 2, lines 43-45). ***The Cathey reference expressly states that this solution has a BPSG to TEOS selectivity ratio of only 6.3:1; not 27:1 to 55:1.*** (Cathey, col. 2, lines 58-59). Clearly, the solution of the Cathey reference does not possess a similar selectivity ratio as the etchant solution of the present invention. As Cathey does not teach or suggest every limitation of independent claim 9 of the presently claimed invention, appellants respectfully submit that independent claim 9 is not rendered obvious the Cathey reference. As such, independent claim 9 is allowable.

Claims 10 through 15 are each allowable as depending from independent claim 9.

Claim 13 is further allowable as the Cathey reference does not teach or suggest the acetic acid is in a volumetric ratio with the hydrofluoric acid at about 1:1 to about 500:1. Instead, the Cathey

reference only discloses a solution containing a ratio of acetic acid to hydrofluoric acid of 2:1. Cathey does not teach or suggest increasing the ratio of acetic acid in the solution. By contrast, the Cathey reference teaches that acetic acid is not an important component of the solution and thus teaches away from the presently claimed invention.

Claim 14 is further allowable as the Cathey reference does not teach or suggest the acetic acid is in a volumetric ratio with the hydrofluoric acid at about 10:1 to about 100:1. Instead, the Cathey reference only discloses a solution containing a ratio of acetic acid to hydrofluoric acid of 2:1. Cathey does not teach or suggest increasing the ratio of acetic acid in the solution. By contrast, the Cathey reference teaches that acetic acid is not an important component of the solution and thus teaches away from the presently claimed invention

Claim 15 is further allowable as the Cathey reference does not teach or suggest the organic acid comprises glacial acetic acid and the fluoride-containing solution comprises 40% ammonium fluoride by weight in water.

CONCLUSION

Appellants request the reversal of the rejection of currently pending claims 1 through 4 and 6 through 15 for the reasons set forth above.

APPENDIX

Appealed claims 1 through 4 and 6 through 15 are attached hereto as the Appendix.

Respectfully submitted,



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Date: September 18, 2001
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APPENDIX

1. An etchant solution which selectively etches borophosphosilicate glass over tetraethyl orthosilicate, said etchant solution comprising an organic acid and a fluoride-containing solution provided in a selected volumetric ratio relative to one another, wherein the selected volumetric ratio of the organic acid to the fluoride-containing solution is about 10:1 to about 500:1.

2. The etchant of claim 1, wherein said organic acid is selected from the group consisting of acetic acid, formic acid, and oxalic acid.

3. The etchant of claim 1, wherein said fluoride-containing solution is selected from the group consisting of hydrofluoric acid and ammonium fluoride.

4. The etchant of claim 1, wherein said organic acid comprises glacial acetic acid and said fluoride-containing solution comprises 49% hydrofluoric acid by weight in water.

6. The etchant of claim 4, wherein said acetic acid is in a volumetric ratio with said hydrofluoric acid at about 10:1 to about 100:1.

7. The etchant of claim 1, wherein said organic acid comprises glacial acetic acid and said fluoride-containing solution comprises 40% ammonium fluoride by weight in water.

8. The etchant of claim 1, wherein said etchant solution exhibits a selectivity ratio of borophosphosilicate glass to tetraethyl orthosilicate between about 27:1 and 55:1.

9. An etchant solution which selectively etches borophosphosilicate glass over tetraethyl orthosilicate, said etchant solution comprising an organic acid and a fluoride-

containing solution, wherein the etchant solution exhibits a selectivity ratio of borophosphosilicate glass to tetraethyl orthosilicate between about 27:1 and 55:1.

10. The etchant of claim 9, wherein the organic acid is selected from the group consisting of acetic acid, formic acid, and oxalic acid.

11. The etchant of claim 9, wherein the fluoride-containing solution is selected from the group consisting of hydrofluoric acid and ammonium fluoride.

12. The etchant of claim 9, wherein the organic acid comprises glacial acetic acid and the fluoride-containing solution comprises 49% hydrofluoric acid by weight in water.

13. The etchant of claim 12, wherein the acetic acid is in a volumetric ratio with the hydrofluoric acid at about 1:1 to about 500:1.

14. The etchant of claim 12, wherein the acetic acid is in a volumetric ratio with the hydrofluoric acid at about 10:1 to about 100:1.

15. The etchant of claim 9, wherein the organic acid comprises glacial acetic acid and the fluoride-containing solution comprises 40% ammonium fluoride by weight in water.